ETS-4: Maxwell's Zeolite

Scottish physicist James Clerk Maxwell (1831–1879) discussed a mythical device that could separate molecules by temperature, a concept now known as Maxwell's demon. Maxwell used this idea to explore how sorting molecules by size would violate the second law of thermodynamics. If one did have a Maxwell's demon, a more useful task for it would likely be to separate molecules by size. This would allow mixtures to be separated into pure substances, and would facilitate removal of dangerous contaminants from valuable materials. In some cases, molecular separations can be performed using zeolites and similar materials. Zeolites are composed of linked tetrahedral SiO_4 and AlO_4 species, arranged in rings to create a framework of molecule-sized cavities. Related zeolitic materials may use other tetrahedral atoms to build the framework. Molecules can access these cavities or pores, under two conditions: if they can pass through the appropriate rings in the framework and these rings are not blocked by other species in the material, such as cations. If the ring size in a material matches the needs for a particular chemical separation, the material may be appropriate. Chemical modifications, such as ion exchange or changing the framework composition can sometimes influence the pore size. So, occasionally it is possible to modify a zeolite to a particular separation. However, this does not allow what Maxwell might envision, where the pore size can be adjusted over a wide range to suit the desired process, in effect a Maxwell's demon for size separations. This exact capability has now been demonstrated in material ETS-4 [1]. ETS-4 can be processed in such a way so that the pore sizes can be tuned for particular separations.

ETS-4 is a titanosilicate material invented by Engelhard in the 1980s [2]. ETS-4 differs from most zeolitic materials in a number of ways. Chemically, it is an oxide of Ti and Si, while the majority of zeolitic materials are oxides of Al and Si. Structurally, the material is composed of both tetrahedral TiO_4 and octahedral TiO_6 units, as well as SiO_4 units. Finally, most zeolitic materials hydrate and dehydrate reversibly or are destroyed during dehydration. ETS-4, at least in some ion-exchanged forms, can be induced to dehydrate irreversibly and without destruction of the pores. Dehydration reduces the average pore opening size. Thus it is possible to tune the zeolite to accept molecules of a particular size by changing the level of dehydration. The temperature to which the material is exposed in turn dictates the amount of dehydration. In 1999, the Advanced Technology Program funded Engelhard to exploit this effect, which Engelhard calls the Molecular Gate®, to develop methods for separating oxygen from air, a process with useful applications for prevention of pollution as well as medical and other industrial applications.

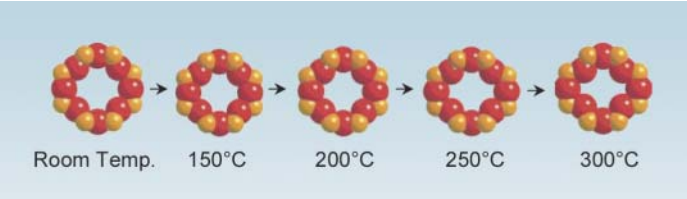

FIGURE 1. Size of the eight-ring pore opening in ETS-4 as a function of dehydration temperature.

The mechanism behind the Molecular Gate® effect was demonstrated crystallographically using data from the BT-1 neutron powder diffractometer. Pores in ETS-4 must be accessed via a ring of eight Si and Ti atoms, each linked by oxygen atoms. This ring is commonly called an eight-ring, despite the fact that it is actually composed of sixteen atoms. In Fig. 1, the size of this eight-ring is shown as a function of dehydration temperature. The actual size of molecules that can be admitted via this opening are dictated by the van der Waals radii of the O atoms in the eight-ring and the van der Waals dimensions of the molecule to be admitted. Since accurate determination of oxygen atom siting is needed, and since ETS-4 does not form single crystals, neutron powder

TABLE 1. Eight-ring opening as a function of dehydration temperature. Distances are the pore-openings separating van der Waals radii between opposite O5 (D_1), O1 (D_2) and O2 (D_3) atom pairs (see FIGURE 2).

van der Waals opening (Å)	Dehydration Temperature, °C				
	RT	150	200	250	300
D_1	4.27	3.97	3.95	3.94	3.90
D_2	4.43	4.02	4.09	4.57	4.57
D_3	3.61	3.28	3.29	3.27	2.77

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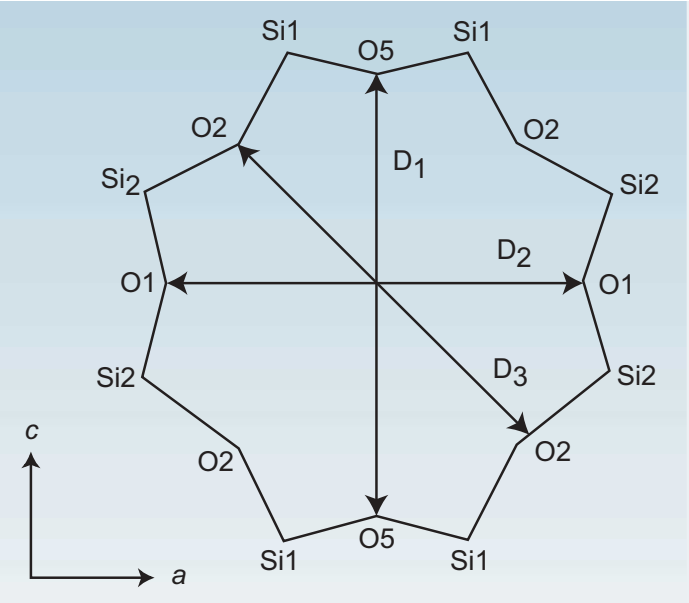

FIGURE 2. Atom and pore-opening distance labeling scheme in the eight-ring opening of ETS-4.

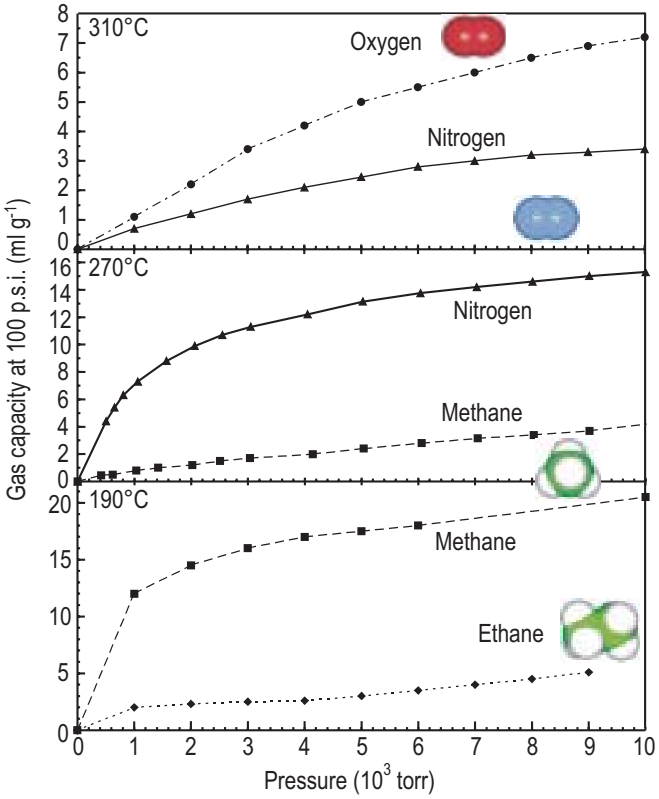

FIGURE 3. Adsorption of selected molecules as a function of dehydration temperature.

diffraction measurements are the only way to obtain accurate measurements of the ring openings as a function of dehydration temperature. Measurements of the eight-ring opening from Rietveld refinements are shown in Table 1, relative to the distances diagrammed in Fig. 2.

The proof that dehydration indeed does change the pore access is demonstrated by adsorption isotherms, shown in Fig. 3. The separation shown in the top of this figure, between O_2 and N_2, shows how precisely the pore sizes can be adjusted. The difference in van der Waals radius between oxygen and nitrogen is only 0.1 Å.

References

[1] S. M. Kuznicki, V. A. Bell, S. Nair, H. W. Hillhouse, R. M. Jacubinas, C. M. Braunbarth, B. H. Toby, and M. Tsapatsis, Nature **412**, 720 (2001).

[2] S. M. Kuznicki, US Patent 4938939 (1990).